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Recursive calculation of high-order molecular response properties

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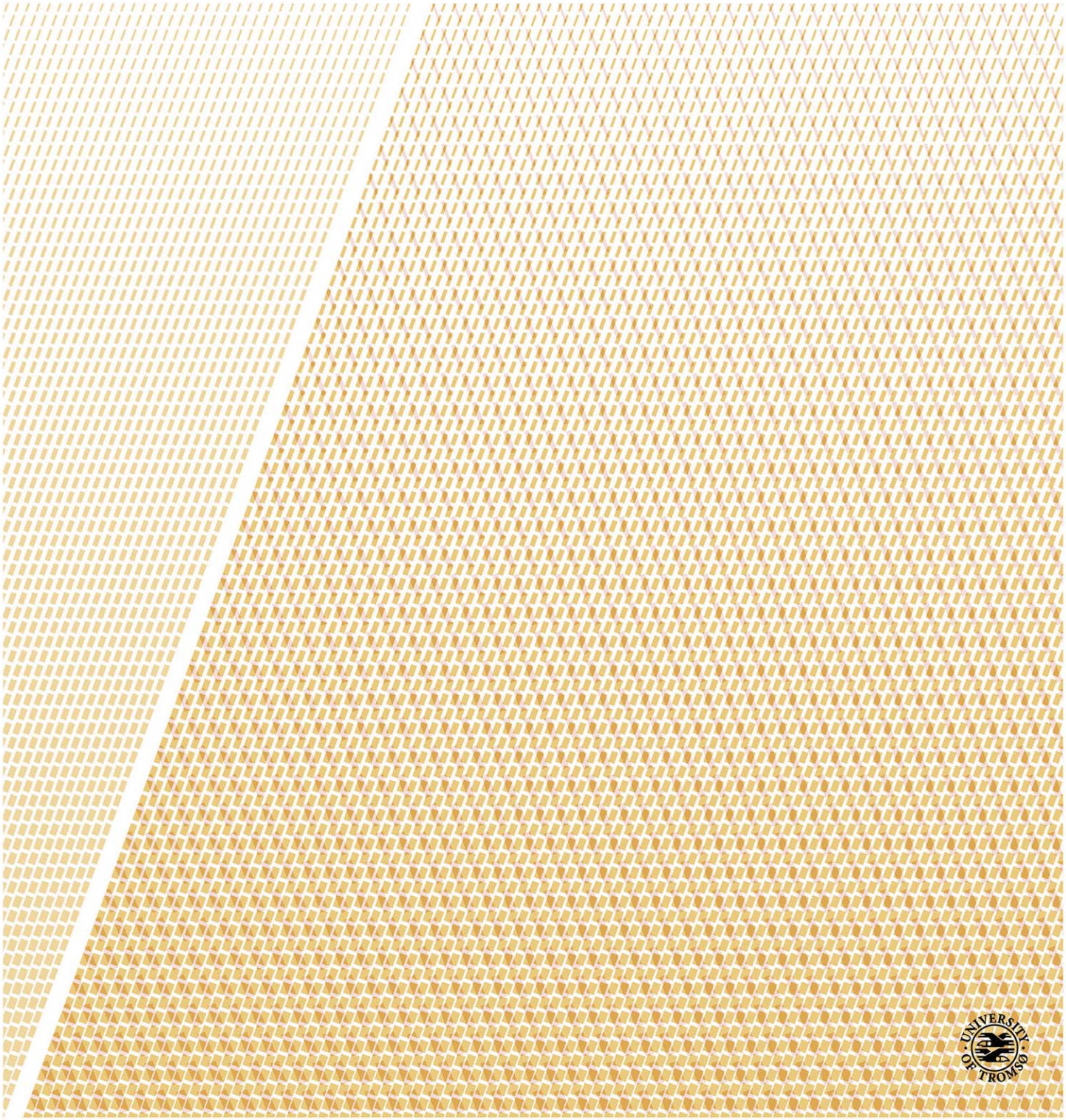

Abstract

This thesis presents the implementation and application of a computer program for the open-ended calculation of response properties of molecular systems. Using recursive programming techniques, a recently published formulation of response theory can be implemented in a manner that allows the calculation of response properties to arbitrary order. The limitations of the code are dictated by the limitations of connected modules that provide perturbed one- and two-electron integral contributions and exchange and correlation contributions. The properties available from the code are used for a selection of applications: The calculation of the cubic force constants of the second hyperpolarizability of HSOH at the Hartree-Fock level, cubic and quartic force constants of various organic molecules at the density-functional theory (DFT) level, pure vibrational contributions to the polarizability and first hyperpolarizability of retinal and retinal derivatives at the DFT level, and hyper-Raman spectra of two conformations of retinal at the DFT level.

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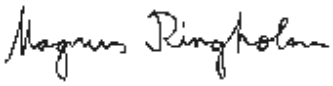

Magnus Ringholm

Contents

List of papers

This thesis is based on the following scientific papers:

I A general, recursive and open-ended response code: M. Ringholm, D. Jonsson, and K. Ruud, *Submitted to J. Comput. Chem.*

II Analytic cubic and quartic force fields using density-functional theory: M. Ringholm, D. Jonsson, R. Bast, B. Gao, A. J. Thorvaldsen, U. Ekström, T. Helgaker, and K. Ruud, *Submitted to J. Chem. Phys.*

III Analytic density-functional theory calculations of pure vibrational hyperpolarizabilities: The first dipole hyperpolarizability of retinal and related molecules: B. Gao, M. Ringholm, R. Bast, K. Ruud, A. J. Thorvaldsen, and M. Jaszuński, *Submitted to J. Phys. Chem.*

IV Analytic density-functional theory hyperpolarizability gradients: The hyper-Raman spectra of all-trans- and 11-cis-retinal: M. Ringholm, R. Bast, L. Oggioni, U. Ekström, and K. Ruud, *Submitted to J. Phys. Chem.*

Not included in the thesis:

I Hyper Raman spectra calculated in a time-dependent Hartree-Fock method, A. Mohammed, H. Ågren, M. Ringholm, A. J. Thorvaldsen, and K. Ruud, *Mol. Phys.* **110**, 2315 (2012)

Chapter 1

Introduction

Computational chemistry is a valuable complement to experimental chemistry. By the creation of computer programs based on chemical theory, the researcher is able to use simulation to supplement or surpass experimental methods, gaining a greater understanding of the phenomena being studied due to the analytical quality of the theory from which the program was created. Computational methods lend themselves excellentely to studies of a wide range of molecular systems without many of the limitations that can constrain experimental work. Calculations can be done on a wide range of compounds for which experiments would have been impractical or economically unfeasible: The compounds may be challenging to synthesize, or there may be a large number of candidate molecules for a particular application, making a complete experimental analysis difficult. In addition, the experimental work may be impossible due to the nature of the experimental conditions, for example extreme conditions such as the ones found in stellar matter [1], or dangerous or expensive compounds may be involved.

The computational methods available today are routinely able to describe various chemical situations with ever increasing accuracy. Still, there is a large number of phenomena or molecular systems for which an adequate computational tool is not yet available. Therefore, a lot of effort has been put into the creation of programs that can manage such calculations. Concurrently, the computational capacity has been increasing steadily since the beginning of the field of computational chemistry, meaning that both software and hardware development expand the range of applications for computational chemistry.

The behavior of molecular systems can be studied in a wide range of external conditions, such as being subjected to electric or magnetic fields or

being considered at a particular temperature. The properties that the system can show under these conditions vary widely in nature and complexity, and although many of them are now considered to be well understood and readily calculated, there is still a great number of properties to be explored and made available for calculation. These properties can be used in the simulation of a large selection of spectroscopical processes, providing the researcher with a better understanding of phenomena encountered in current chemical research.

The principal aim of this doctoral thesis has been the creation of a program to allow analytic calculations of molecular properties for which such calculations are difficult to the extent that they have previously rarely or never been done. Based on a recently developed theoretical work[2], we have developed a methodology that allows this and created a program in which this methodology is implemented. We have then used this program for the calculation of various molecular properties, some of which are complicated and have not been calculated before, or have until now only been possible to calculate through the application of numerical methods.

The rest of the text is organized as follows: In Chapter 2, we present the theory that is relevant to the thesis. In Chapter 3, we give an overview of the papers included in this thesis. Finally, there will be a brief discussion of future work in Chapter 4.

Chapter 2

Theory

In this chapter, we provide the theoretical foundation on which the thesis is built. In Section 2.1, we give an introduction to the basic concepts and methods of quantum chemistry by presenting the fundamental topics and outlining the Hartree-Fock and density-functional theory approaches. In Section 2.2, we introduce molecular properties and response theory. We proceed to give an overview of the basics of molecular vibrations and related topics in Section 2.3. In Section 2.4, we present some of the central programming techniques used in the development of the general open-ended response code which is the main outcome of this work. In all sections, we will use atomic units unless otherwise stated.

2.1 Quantum chemistry

This section will give an introduction to the concepts of quantum chemistry that are most important in this thesis. It will cover the fundamentals of quantum chemistry and present the Hartree-Fock (HF) method and density-functional theory (DFT). Significant parts of this section has been based on the textbook material[3] by Peter Atkins and Ronald Friedman and the introduction to the doctoral thesis by Andreas J. Thorvaldsen[4]. Some parts of this section follow the introduction to the doctoral thesis by Arnfinn H. Steindal[5].

At the core of quantum chemistry is the Schrödinger equation. The state of a quantum-mechanical system is described by a wavefunction $\Psi(\mathbf{r})$, where $\mathbf{r}$ is a set of coordinates (generally spatial and spin coordinates) that describes the system. The time-dependent Schrödinger equation has the form

$$i\frac{\partial}{\partial t}\Psi = \hat{H}\Psi \tag{2.1}$$

where we introduced the Hamiltonian operator $\hat{H}$, which is the operator for the total energy of the system. For a collection of particles p of the system, with positions $\mathbf{r}_p$, masses m_p and charges q_p, for which a collection of distinct particle pairs (p, q) can be considered, the Hamiltonian takes the form

$$\hat{H} = \sum_p \hat{T}_p + \sum_{p>q} \hat{V}_{pq}, \tag{2.2}$$

where the kinetic energy $\hat{T}_p$ and potential energy $\hat{V}_{pq}$ operators have been introduced and are given by

$$\hat{T}_p = -\frac{1}{2m_p}\nabla_p^2 \tag{2.3}$$

and

$$\hat{V}_{pq} = \frac{q_p q_q}{||\mathbf{r}_p - \mathbf{r}_q||}. \tag{2.4}$$

If the potential energy does not depend on time, the Schrödinger equation can be separated into parts that depend on time and space alone, respectively. The time-independent Schrödinger equation is the resulting spatial part of this separation, and it has the form

$$\hat{H}\psi = E\psi, \tag{2.5}$$

where the energy E of the system is an eigenvalue of $\hat{H}$, with ψ being an eigenfunction of $\hat{H}$.

The energy of the system is an example of an observable, which is a property of the system that it is possible to measure. In a series of measurements of an observable represented by the operator $\hat{\Omega}$, the mean value of the measurements is called the expectation value $\langle\Omega\rangle$ and is given by

$$\langle\Omega\rangle = \frac{\int \psi^*\hat{\Omega}\psi \mathrm{d}\tau}{\int \psi^*\psi \mathrm{d}\tau} = \frac{\langle\psi|\hat{\Omega}|\psi\rangle}{\langle\psi|\psi\rangle}, \tag{2.6}$$

where we have introduced the commonly used bra-ket notation

$$\langle\psi|\hat{\Omega}|\psi\rangle = \int \psi^*\hat{\Omega}\psi \mathrm{d}\tau. \tag{2.7}$$

The ket $|\psi\rangle$ denotes the state of the system, and $\langle\psi| = |\psi\rangle^\dagger$, where the superscript † denotes taking the Hermitian adjoint. The state $|\psi\rangle$ is a vector in a space of states, and it is possible to express it as a linear combination of orthonormal basis vectors $|n\rangle$ that completely span this space, so that

$$|\psi\rangle = \sum_n c_n |n\rangle, \tag{2.8}$$

where c_n are the expansion coefficients.

In the Born-Oppenheimer approximation [6], we consider the nuclei of a molecular system to be fixed in space, so that they give rise to a static electric potential. The validity of this approximation is based on the fact that the nuclei are much heavier than the electrons, and therefore, electrons can respond practically instantaneously to any changes in the nuclear positions. The Hamiltonian of the molecular system is then written as a kinetic term $\hat{T}_n$ involving only the nuclei, and an electronic Hamiltonian $\hat{H}^{\text{el}}$, so that

$$\hat{H} = \sum_n \hat{T}_n + \hat{H}^{\text{el}}, \tag{2.9}$$

where

$$\hat{H}^{\text{el}} = \sum_{n>m} \hat{V}_{nm} + \sum_e \left(\hat{T}_e + \sum_n \hat{V}_{en} \right) + \sum_{f,e>f} \hat{V}_{ef} \tag{2.10}$$

for nuclei m and n and electrons e and f, where the first term on the right-hand side is a nuclear repulsion term commmonly denoted by h_{nuc}, the terms in the summation over e are one-electron terms that are denoted by $\hat{h}$, and the last term is a two-electron term that we denote by $\hat{g}$.

When trying to determine the wavefunction at some level of theory, a trial wavefunction ψ_t can be introduced as a guess or estimate for the true wavefunction or optimal wavefunction at that level of theory. Let E_0 be the lowest energy of a system described by a Hamiltonian $\hat{H}$. The Rayleigh ratio $\mathcal{E}$ is then given by

$$\mathcal{E} = \frac{\langle\psi_t|\hat{H}|\psi_t\rangle}{\langle\psi_t|\psi_t\rangle}. \tag{2.11}$$

Then, for any ψ_t, the variational principle states that

$$\mathcal{E} \geq E_0, \tag{2.12}$$

meaning that a trial wavefunction will never have an energy lower than that of the true ground-state energy of the system. Furthermore, $\mathcal{E} = E_0$ if

and only if ψ_t is the true ground-state wavefunction ψ of the system. The variational principle can be used in determining the optimal wavefunction at some level of theory in what is called the variational method, where one tries to determine a wavefunction ψ_t so that the Rayleigh ratio is minimzed.

The Schrödinger equation can not be solved analytically for systems that contain more than one electron and one nucleus. A common way of addressing this is to use self-consistent field (SCF) approaches. The starting point for SCF methods is the representation of the wavefunction as a Slater determinant. We first introduce the concept of a molecular orbital (MO) to represent the electronic wavefunction. A molecular orbital ϕ_k can contain up to two electrons, where, in the case of double occupancy, the electrons will have spin states that are opposite to each other. In the linear combination of atomic orbitals (LCAO) approximation, the MOs are represented as linearly independent combinations of atomic orbitals

$$\phi_k = \sum_{\mu} C_{\mu k} \chi_{\mu}, \tag{2.13}$$

where $C_{\mu k}$ is an expansion coefficient and χ_μ is an atomic orbital (AO). The atomic orbitals are one-electron atomic wavefunctions centered on the nuclei, and they can in turn be represented by basis functions that together attempt to imitate the true shape of the atomic wavefunction. With a Slater determinant [7], the N-electron wavefunction is represented as a combination of MOs $\phi_{i\tau}(n)$ for each electron n, where a subscript τ denotes a spin state (α or β), so that the Slater determinant representing the wavefunction ψ is given by

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{1\alpha}(1) & \phi_{1\beta}(1) & \cdots & \phi_{\frac{N}{2}\beta}(1) \\ \phi_{1\alpha}(2) & \phi_{1\beta}(2) & \cdots & \phi_{\frac{N}{2}\beta}(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{1\alpha}(N) & \phi_{1\beta}(N) & \cdots & \phi_{\frac{N}{2}\beta}(N) \end{vmatrix}, \tag{2.14}$$

where $\frac{1}{\sqrt{N!}}$ is a normalization factor. Using a determinant to represent the wavefunction ensures that the products obtained are antisymmetric, thus automatically supporting the Pauli exclusion principle[8].

2.1.1 Hartree-Fock theory

Hartree-Fock (HF) theory[9] is one of the most common examples of an SCF method, and is the result of applying the variational method to the Slater

determinant of eqn. (2.14) using the electronic Hamiltonian of eqn. (2.10). The energy can then be evaluated from the expression

$$E = h_{\text{nuc}} + \sum_k \left\langle \phi_k \left| -\frac{1}{2}\nabla^2 - \sum_n \frac{q_n}{||\mathbf{r} - \mathbf{r}_\text{n}||} \right| \phi_k \right\rangle + \\ \frac{1}{2}\sum_{jk} \int\int \phi_j^*(\mathbf{r}_1)\phi_k^*(\mathbf{r}_2)\frac{1}{r_{12}} \left[\phi_j(\mathbf{r}_1)\phi_k(\mathbf{r}_2) - \phi_k(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\right] \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \tag{2.15}$$

In eqn. (2.15), the first term on the second line is called the Coulomb repulsion term, dealing with the electrostatic repulsion between the charge distribution of each electron and the charge distributions of the other electrons, so that this effect deals with the "mean effect" of the other electrons on each electron. The second term is called the exchange interaction term, which is a quantum effect that is a consequence of the Pauli exclusion principle for identical fermions.

Using $\mathbf{C}$ to represent the matrix of all the AO expansion coefficients of eqn. (2.13), eqn. (2.15) can be reformulated in matrix form as

$$E = h_{\text{nuc}} + \text{Tr}(\mathbf{C}^\dagger\mathbf{H}\mathbf{C}) + \frac{1}{2}\text{Tr}(\mathbf{C}^\dagger\mathbf{G}(\mathbf{C}\mathbf{C}^\dagger)\mathbf{C}, \tag{2.16}$$

where the one-electron matrix $\mathbf{H}$ has been introduced as

$$H_{\mu\nu} = \left\langle \chi_\mu \left| \hat{h} \right| \chi_\nu \right\rangle = \left\langle \chi_\mu \left| -\frac{1}{2}\nabla^2 - \sum_n \frac{q_n}{||\mathbf{r} - \mathbf{r}_\text{n}||} \right| \chi_\nu \right\rangle, \tag{2.17}$$

where $\hat{h}$ is the one-electron part of eqn. (2.10). Correspondingly, the two-electron matrix $\mathbf{G}(\mathbf{A})$, dependent on some matrix $\mathbf{A}$, is defined as

$$\mathbf{G}(\mathbf{A})_{\mu\nu} = \sum_{\rho\sigma} \mathbf{G}_{\mu\nu,\rho\sigma}\mathbf{A}_{\sigma\rho}, \tag{2.18}$$

corresponding to the integral of $\hat{g}$ of eqn. (2.10), where

$$\mathbf{G}_{\mu\nu,\rho\sigma} = \int\int \chi_\mu^*(\mathbf{r}_1)\chi_\rho^*(\mathbf{r}_2)\frac{1}{r_{12}} \left[\chi_\nu(\mathbf{r}_1)\chi_\sigma(\mathbf{r}_2) - \chi_\sigma(\mathbf{r}_1)\chi_\nu(\mathbf{r}_2)\right] \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2. \tag{2.19}$$

The orthonormality requirement of the orbitals can be written on the form

$$\langle\phi_j|\phi_k\rangle = \delta_{jk} \rightarrow \mathbf{C}^\dagger\mathbf{S}\mathbf{C} = \mathbf{1}, \tag{2.20}$$

where the overlap matrix $\mathbf{S}$ was introduced and is given by

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle. \tag{2.21}$$

With an eye to the formalism used in the papers of this thesis, we introduce the density matrix $\mathbf{D} = \mathbf{C}\mathbf{C}^\dagger$, for which the dimensionality corresponds directly to the basis functions of the atomic orbitals. Eqn. (2.16) can in the density matrix formulation be written as

$$E = h_{\text{nuc}} + \text{Tr}(\mathbf{H}\mathbf{D}) + \frac{1}{2}\text{Tr}(\mathbf{G}(\mathbf{D})\mathbf{D}. \tag{2.22}$$

Pre- and postmultiplying eqn. (2.20) by $\mathbf{C}$ and $\mathbf{C}^\dagger$, respectively, the idempotency condition

$$\mathbf{D}\mathbf{S}\mathbf{D} = \mathbf{D}, \tag{2.23}$$

defining a constraint on constraint on $\mathbf{D}$, is obtained. It can be shown[10] that the variational condition in this formulation, under the constraint of eqn. (2.23), can be written as

$$\mathbf{F}\mathbf{D}\mathbf{S} = \mathbf{S}\mathbf{D}\mathbf{F}, \tag{2.24}$$

where the Fock matrix $\mathbf{F} = \mathbf{H} + \mathbf{G}(\mathbf{D})$ was introduced.

The HF procedure then begins by choosing basis functions to represent the atomic orbitals, and they are used to calculate $\mathbf{S}$ from eqn. (2.21). Next, an initial guess of $\mathbf{D}$ is made, and $\mathbf{F}$ can then be calculated. The energy can be calculated from eqn. (2.22). Eqn. (2.24) can then be solved for an updated $\mathbf{D}$, which in turn can be used to calculate an updated $\mathbf{F}$, and this iterative procedure can be continued. The new $\mathbf{D}$ and the associated energy from eqn. (2.22) can be compared with $\mathbf{D}$ and the associated energy obtained in the previous iteration until the difference between the present and previous iteration is small enough that self-consistency can be said to have been reached.

2.1.2 Density-functional theory

As discussed in the previous section, the Coulomb term in eqn. (2.15) describes the mean Coulomb repulsion on an electron from the other electrons in the molecule. What is neglected with this method is the instantaneous repulsion between the electrons. This effect is commonly called electronic correlation, and the Hartree-Fock method is commonly referred to as an uncorrelated method (that is, not including electronic correlation). This is

despite the fact that electronic exchange, which is included in Hartree-Fock theory, is a form of electronic correlation. Henceforth, we will take the electron correlation energy (or just "correlation energy" for short) to mean the difference in energy obtained by the uncorrelated HF method and the energy obtained from a correlated method, which is a method that tries to describe the electronic correlation that HF theory does not.

There are several ways of introducing correlation in the theory. One can for example use Slater determinants that include excited states, or one can use perturbation theory to make corrections to the wavefunction. However, this section will be restricted to Kohn-Sham density-functional theory (DFT)[11], which is a method where the spatial electron density is the basic concept from which the behavior of the system is found through the formulation of a functional for the system's energy.

Let the ground-state spatial electronic density $\rho(\mathbf{r})$ of some wavefunction be defined by

$$\rho(\mathbf{r}) = C \int |\psi|^2 \mathrm{d}\tau, \tag{2.25}$$

where C is some normalization constant. Then, the Hohenberg-Kohn theorem states that there is a one-to-one relation between $\rho(\mathbf{r})$ and the potential functions $v(\mathbf{r})$ in the electronic Hamiltonian, so that for a given electronic ground-state density, there exists exactly one Hamiltonian. In molecular systems, the external potential $v(\mathbf{r})$ is defined by the Coulomb attractions

$$v(\mathbf{r}) = -\sum_n \frac{q_n}{||\mathbf{r} - \mathbf{r}_n||} \tag{2.26}$$

between the electrons and the nuclei. If, furthermore, the ground state is non-degenerate, then there exists a variational energy functional $E_v[\rho]$ that describes the energy of the system, so that for the true density $\rho(\mathbf{r})$, the energy $E_v[\rho]$ corresponds to the ground state energy of the system. A functional is a function which takes another function as argument, which in turn can take another function or scalar as its argument. The general form of $E_v[\rho]$ is

$$E_v[\rho] = h_{\mathrm{nuc}} + \int v(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r} + (T+V)[\rho], \tag{2.27}$$

where $T[\rho]$ and $V[\rho]$ are functionals for the electronic kinetic energy and Coulomb and exchange repulsion, respectively. In eqn. (2.27), the form of the nuclear repulsion h_{nuc} and electron-nuclear attraction $\int v(\mathbf{r})\rho(\mathbf{r})$ contributions are known, but $T[\rho]$ and $V[\rho]$ are not known.

A viable approach to deal with the unknown functionals $T[\rho]$ and $V[\rho]$ is to identify large analytic or well-defined parts of them from other levels of theory, in order to make the unknown parts of $T[\rho]$ and $V[\rho]$ smaller. Hartree-Fock theory, for instance, contains both a kinetic energy term $T_s[\rho]$ between noninteracting electrons, and a Coulomb electron-electron repulsion term, $J[\rho]$, where $J[\rho]$ is written as

$$J[\rho] = \frac{1}{2}\int \rho(\mathbf{r}_1)\frac{1}{r_{12}}\rho(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2. \tag{2.28}$$

In Kohn-Sham DFT [11], $T_s[\rho]$ and $J[\rho]$ are separated from $T[\rho]$ and $V[\rho]$, respectively and the remainder of $T[\rho]$ and $V[\rho]$ is combined into the exchange-correlation functional $E_{\mathrm{xc}}[\rho]$, so that

$$(T+V)[\rho] = E_{\mathrm{xc}}[\rho] + T_s[\rho] + J[\rho]. \tag{2.29}$$

Inserting this into eqn. (2.27), the Kohn-Sham density functional can be written as

$$E_v[\rho] = h_{\mathrm{nuc}} + \int v(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r} + (T_s + J)[\rho] + E_{\mathrm{xc}}[\rho]. \tag{2.30}$$

A vast amount of work has been done in trying to find forms of $E_{\mathrm{xc}}[\rho]$ that yield accurate results. It is possible to classify these functionals obtained into broad categories. In the simplest approximation, it is assumed that $E_{\mathrm{xc}}[\rho]$ can be described simply as the integral over some function of the density $\rho(\mathbf{r})$ alone. This approximation is called the local density approximation (LDA). It is also possible to include the gradient of $\rho(\mathbf{r})$ in the function to be integrated, in what is called the generalized gradient approximation (GGA). In meta-GGA functionals, the kinetic energy density[12] $\tau(\mathbf{r})$ of the occupied orbitals is also included, where

$$\tau(\mathbf{r}) = \frac{1}{2}\sum_{\alpha}^{\text{occupied}} |\nabla\phi_\alpha(\mathbf{r})|^2. \tag{2.31}$$

Hartree-Fock theory includes electronic exchange effects. Some fraction of this effect can be included explicitly in $E_{\mathrm{xc}}[\rho]$. The functional thus obtained is called a hybrid functional. Finally, some fraction of correlation effects from other levels of theory can be separated out from $E_{\mathrm{xc}}[\rho]$ in addition to taking the aforementioned exhange contribution from HF theory. A functional incorporating both these elements is called a double hybrid functional. The increasing complexity of the various theories to determine $E_{\mathrm{xc}}[\rho]$ will in general yield increasingly accurate results. This progression

has been likened to a "Jacob's ladder" stretching from HF theory to the "heaven of chemical accuracy"[13].

2.2 Molecular properties and response theory

In this section, we turn to the discussion of molecular properties and the theory necessary for their calculation. In this work, a molecular property is taken to be some feature of a molecular system that is related to the way the system acts when subjected to one or a collection of internal or external factors that could be said to change or *perturb* the state of the system. Such a perturbation could for instance be an electromagnetic field, or shifting the molecular geometry from its equilibrium position.

We begin by showing that a description of the behavior of the perturbed system can be obtained from considering the so-called quasienergy of the system. Using the quasienergy framework, it will be shown that molecular properties can be described using response theory. A presentation of some of these properties and their possible applications will be given in the final part of this section. The theory presented in this section follows closely both the work of Ove Christiansen and co-workers [14] and the introduction to the doctoral thesis of Andreas J. Thorvaldsen [4].

2.2.1 The wavefunction in perturbing fields and the quasienergy

When a molecular system is subjected to one or more external perturbing fields, this can be described by adding a potential $\hat{V}^t$ to the Hamiltonian $\hat{H}$ of the isolated system. The perturbing fields can oscillate with their respective frequencies, or they can be static. As will be shown below, these frequencies can form the basis of a Fourier decomposition, and with an eye to this, we denote by Ω the set of all integer multiples of the frequencies of the perturbing fields.

In general, because of non-stationary fluctuations, the state of the system is dependent on when the perturbation came into effect, i.e. when (and how gradually or suddenly) it was switched on. However, in the following we disregard this effect, and consider the perturbation to always have been on, so that no such effects need to be considered. Furthermore, we impose on the wavefunction for the system, denoted by $\tilde{\psi}$, that it must be possible to separate it into a product

$$\tilde{\psi} = e^{-iF(t)}\psi \tag{2.32}$$

of a phase factor $e^{-iF(t)}$ (with a presently unspecified time-dependent function $F(t)$) and a phase-isolated wavefunction ψ, and that the phase-isolated part is quasi-periodic with respect to the perturbing fields. This means that ψ can be written as a Fourier decomposition

$$\psi = \sum_{w \in \Omega} e^{i\omega t} \psi_\omega, \tag{2.33}$$

where the set Ω defined above is applied. For a general collection of perturbations, this means that ψ can be considered to be periodic to arbitrarily high precision - hence the term "quasi-periodic". The reason for this is that the frequency components of the perturbing fields may in general not share a common divisor. Consequently, there may not be a fundamental frequency of which all field frequencies is a multiple, so that a Fourier decomposition in Ω is not necessarily periodic. However, in practice, if the frequencies are specified to arbitrary but finite precision (for example limited by machine precision), there must exist such a fundamental frequency, and both the perturbations and any Fourier decomposition in Ω must therefore be periodic.

The time-dependent Schrödinger equation can then be formulated as

$$\left(\hat{H} + \hat{V}^t\right) \tilde{\psi} = i \frac{\partial}{\partial t} \tilde{\psi}. \tag{2.34}$$

Inserting eqn. (2.32), the expression

$$\left(\hat{H} + \hat{V}^t\right) e^{-iF(t)} \psi = i \frac{\partial}{\partial t} e^{-iF(t)} \psi \tag{2.35}$$

is obtained, where the right-hand side can be expressed as

$$i \frac{\partial}{\partial t} e^{-iF(t)} \psi = e^{-iF(t)} \left(\dot{F}(t) + i \frac{\partial}{\partial t}\right) \psi. \tag{2.36}$$

Setting $\dot{F}(t)$ to be the time-dependent quasienergy $Q(t)$, eqn. (2.35) can be reformulated as the Floquet-Schrödinger equation

$$\left(\hat{H} + \hat{V}^t - i \frac{\partial}{\partial t}\right) |\psi\rangle = Q(t) |\psi\rangle. \tag{2.37}$$

It can be seen from eqn. (2.37) that $Q(t)$ takes on a similar role to the energy, within the perturbational situation and the assumptions made above.

Let $|\delta\tilde{\psi}\rangle$ be a first-order variation of $|\tilde{\psi}\rangle$. From eqn. (2.32), $|\delta\tilde{\psi}\rangle$ can be rewritten as

$$|\delta\tilde{\psi}\rangle = e^{-iF}|\delta\psi\rangle - i\delta F e^{-iF}|\psi\rangle \tag{2.38}$$

Due to the fact that δF and $\delta\psi$ are independent variations, when projecting the variation $|\delta\tilde{\psi}\rangle$ onto eqn. (2.37), the resulting expression can be written as

$$\langle\delta\tilde{\psi}|\left(\hat{H} + \hat{V}^t - i\frac{\partial}{\partial t}\right) - Q(t)|\psi\rangle = 0. \tag{2.39}$$

This expression is also known as Frenkel's time-dependent variational principle [17]. It is known that

$$\langle\tilde{\psi}|\tilde{\psi}\rangle = \langle\psi|e^{iF}e^{-iF}|\psi\rangle = \langle\psi|\psi\rangle = 1. \tag{2.40}$$

Applying a variation to (2.40),

$$\begin{aligned} 0 = \delta(1) &= \delta(\langle\tilde{\psi}|\tilde{\psi}\rangle) \\ &= \langle\delta\tilde{\psi}|\tilde{\psi}\rangle + \langle\tilde{\psi}|\delta\tilde{\psi}\rangle \\ &= \langle\delta\psi|e^{iF}e^{-iF}|\psi\rangle + \langle\psi|e^{iF}e^{-iF}|\delta\psi\rangle + i\delta F\langle\psi|e^{iF}e^{-iF}|\psi\rangle - i\delta F\langle\psi|e^{iF}e^{-iF}|\psi\rangle, \end{aligned} \tag{2.41}$$

where it was used that the variation δF is only dependent on time, and can therefore be moved outside the bracket. Eqn. (2.41) can be written on a form that imposes a requirement on all variations of $|\psi\rangle$, namely that for such a variation $|\delta\psi\rangle$,

$$\langle\delta\psi|\psi\rangle + \langle\psi|\delta\psi\rangle = 0. \tag{2.42}$$

The valid variations $|\delta\psi\rangle$ can be decomposed into a part $|\delta\psi^{\perp}\rangle$ that is orthogonal to $|\psi\rangle$ and a part that is parallel as

$$|\delta\psi\rangle = |\delta\psi^{\perp}\rangle + i\delta\alpha|\psi\rangle, \tag{2.43}$$

where the variation $\delta\alpha$ is real. Projecting $\langle\delta\psi^{\perp}|$ onto eqn. (2.37), it is seen that

$$\langle\delta\psi^{\perp}|\hat{H} + \hat{V}^t - i\frac{\partial}{\partial t}|\psi\rangle = 0. \tag{2.44}$$

Applying eqn. (2.43) to eqn. (2.42), we obtain

$$\langle\delta\psi^{\perp}|\psi\rangle = 0 \tag{2.45}$$

If the real and imaginary orthogonal variations of the variational parameters of $|\psi\rangle$ are independent, there exists an equation which is similar to (2.44), but where the variation was $i\langle\delta\psi^{\perp}|$. This last result and eqn. (2.44) can be formulated as

$$\mathrm{Re}\langle\delta\psi^{\perp}|\hat{H}+\hat{V}^{t}-i\frac{\partial}{\partial t}|\psi\rangle=0, \tag{2.46}$$

where $i\langle\delta\psi^{\perp}|$ can also be used instead of $\langle\delta\psi^{\perp}|$. We note that $i\delta\alpha\langle\psi|\hat{H}+\hat{V}^{t}-i\frac{\partial}{\partial t}|\psi\rangle$ is imaginary, and therefore, using eqn. (2.43), we can bring eqn. (2.46) on the form

$$\mathrm{Re}\langle\delta\psi|\left(\hat{H}+\hat{V}^{t}-i\frac{\partial}{\partial t}\right)|\psi\rangle=0. \tag{2.47}$$

Eqn. (2.47) can then be expanded by its Hermitian conjugate to give

$$\langle\delta\psi|\left(\hat{H}+\hat{V}^{t}-i\frac{\partial}{\partial t}\right)|\psi\rangle+\langle\left(\hat{H}+\hat{V}^{t}-i\frac{\partial}{\partial t}\right)\psi|\delta\psi\rangle=0, \tag{2.48}$$

which can be rearranged into

$$\delta\langle\psi|\left(\hat{H}+\hat{V}^{t}-i\frac{\partial}{\partial t}\right)|\psi\rangle+i\frac{\partial}{\partial t}\langle\psi|\delta\psi\rangle=0, \tag{2.49}$$

used by Langhoff and co-workers [16], and the definition of $Q(t)$ can be recognized, allowing simplification of eqn. (2.49) into

$$\delta Q(t)+i\frac{\partial}{\partial t}\langle\psi|\delta\psi\rangle=0. \tag{2.50}$$

By the Hellmann-Feynman theorem [18][19], differentiation of the energy with respect to a perturbation strength ϵ gives

$$\frac{\mathrm{d}E}{\mathrm{d}\epsilon}=\frac{\mathrm{d}\langle\psi|\hat{H}+\hat{V}^{t}|\psi\rangle}{\mathrm{d}\epsilon}=\langle\psi|\frac{\partial(\hat{H}+\hat{V}^{t})}{\partial\epsilon}|\psi\rangle. \tag{2.51}$$

Applying the same differentiation to the time-dependent quasienergy, the expression

$$\frac{\mathrm{d}Q(t)}{\mathrm{d}\epsilon}=\frac{\mathrm{d}\langle\psi|\hat{H}+\hat{V}^{t}-i\frac{\partial}{\partial t}|\psi\rangle}{\mathrm{d}\epsilon}=\langle\psi|\frac{\partial(\hat{H}+\hat{V}^{t})}{\partial\epsilon}|\psi\rangle-i\frac{\partial}{\partial t}\langle\psi|\frac{\mathrm{d}\psi}{\mathrm{d}\epsilon}\rangle \tag{2.52}$$

is obtained. To continue, it is necessary to take a closer look at the form of the perturbations $\hat{V}^t$. From the previous discussion, the perturbations can be said to be quasi-periodic, so they can be expressed as a Fourier series

$$\hat{V}^t = \sum_{k=-N}^{N} e^{-i\omega_k t}\hat{V}^{\omega_k}, \tag{2.53}$$

where the component $\hat{V}^{\omega_k}$ can be represented as a combination

$$\hat{V}^{\omega_k} = \sum_x \epsilon_x(\omega_k)X, \tag{2.54}$$

where ϵ_x and X are a perturbation strength and operator, respectively. From this, it is seen that

$$\frac{\partial(\hat{H}+\hat{V}^t)}{\partial\epsilon_x(\omega_k)} = Xe^{-i\omega_k t}, \tag{2.55}$$

and this can be inserted into eqn. (2.52), which, finally, can be rearranged into

$$\langle\psi|X|\psi\rangle e^{-i\omega_k t} = \frac{\partial Q(t)}{\partial\epsilon_x(\omega_k)} + i\frac{\partial}{\partial t}\langle\psi|\frac{\mathrm{d}\psi}{\mathrm{d}\epsilon_x(\omega_k)}\rangle \tag{2.56}$$

In the next section, we will show how to develop the theory presented so far into response functions.

2.2.2 Response theory

In this section, we use time-averaging as a crucial step in obtaining response functions. For a function $F(t)$, the time-average $\{F(t)\}_T$ is defined as

$$\{F(t)\}_T = \frac{1}{T}\int_{-T/2}^{T/2} F(t)\mathrm{d}t, \tag{2.57}$$

where the T denotes some period of averaging. We will be concerned with periodic functions (for the purposes of this discussion, we will regard quasi-periodic functions as periodic), and so the T will be taken to mean the period of such functions. We note that the periodic function $\hat{V}^t$ with period T by definition has the property

$$\hat{V}^t(t+T) = \hat{V}^t(t). \tag{2.58}$$

For a periodic function $F(t)$ which is time-differentiated, it can be shown that

$$\left\{\frac{\partial F(t)}{\partial t}\right\}_T = 0 \tag{2.59}$$

Applying eqn. (2.57) to eqn. (2.50) and using eqn. (2.59), the expression

$$\delta\{Q(t)\}_T = 0 \tag{2.60}$$

is obtained, where the time-averaged quasienergy $\{Q(t)\}_T$ was introduced. In the following, we will simply use the term quasienergy for $\{Q(t)\}_T$ to distinguish it from the non-time-averaged or time-dependent quasienergy of the preceding section. An analogous treatment of eqn. (2.56) yields

$$\frac{\mathrm{d}\{Q(t)\}_T}{\mathrm{d}\epsilon_x(\omega)} = \{\langle\psi|X|\psi\rangle e^{-i\omega_x t}\}_T. \tag{2.61}$$

At this point, it is necessary to discuss the periodicity of $|\psi\rangle$. Eqn. (2.50) can be rewritten on the form

$$\delta\langle\psi|H - i\frac{\partial}{\partial t}|\psi\rangle + i\frac{\partial}{\partial t}\langle\psi|\delta\psi\rangle = -\delta\langle\psi|\hat{V}^t|\psi\rangle. \tag{2.62}$$

We will now show that the periodicity of $|\psi\rangle$ is similar to that of $\hat{V}^t$, whose periodicity is stated in eqn. (2.58). Let $\hat{V}^t$ be given to some order n. Then, collecting terms to the same total order of perturbation, only contributions up to and including order $(n-1)$ in the perturbed wavefunction enter into the right-hand side of eqn. (2.62), while the left-hand side also contains terms to order n in the wavefunction. The first-order perturbed wavefunction $|\psi^{(1)}(t)\rangle$ can be written as

$$|\psi^{(1)}(t)\rangle = \sum_{k_1} |\psi^{(1)}(\omega_{k_1})\rangle e^{-i\omega_{k_1} t}, \tag{2.63}$$

and it can be shown by induction that at the second order,

$$|\psi^{(2)}(t)\rangle = \sum_{k_1,k_2} |\psi^{(2)}(\omega_{k_1},\omega_{k_2})\rangle e^{-i(\omega_{k_1}+\omega_{k_2})t}, \tag{2.64}$$

and, in general,

$$|\psi^{(n)}(t)\rangle = \sum_{k_1,k_2,\ldots,k_n} |\psi^{(n)}(\omega_{k_1},\omega_{k_2},\ldots,\omega_{k_n})\rangle e^{-i\sum_{j=1}^{n}\omega_{k_j} t}. \tag{2.65}$$

From the above expressions, it can be seen that the wavefunction is composed of terms that use the same Fourier frequency components as $\hat{V}^t$, and it can therefore be said to be periodic in the same way as $\hat{V}^t$. Therefore, there exists a period over which the time-averaging over terms involving both the wavefunction and $\hat{V}^t$, like in eqn. (2.61), can be done.

In order to complete the connection between the quasienergy and the response properties, we begin by noting that, for an observable represented by a Hermitian operator X, for which the expectation value in absence of any perturbations is represented by $\langle X \rangle$, an expansion in orders of the perturbations to which the system is subjected can always be made, having the form

$$\begin{aligned}\langle \tilde{\psi}|X|\tilde{\psi}\rangle &= \langle \psi|X|\psi\rangle \\ &= \langle X\rangle + \sum_{k_1} e^{-i\omega_{k_1}t} \sum_{y} \langle\langle X;Y\rangle\rangle_{\omega_{k_1}} \epsilon_y(\omega_{k_1}) + \\ &\frac{1}{2}\sum_{k_1,k_2} e^{-i(\omega_{k_1}+\omega_{k_2})t} \sum_{y,z} \langle\langle X;Y,Z\rangle\rangle_{\omega_{k_1},\omega_{k_2}} \epsilon_y(\omega_{k_1})\epsilon_z(\omega_{k_2}) + \ldots .\end{aligned} \tag{2.66}$$

In eqn. (2.66), the linear response function $\langle\langle X;Y\rangle\rangle_{\omega_{k_1}}$, the quadratic response function $\langle\langle X;Y,Z\rangle\rangle_{\omega_{k_1},\omega_{k_2}}$, and so on for higher orders, represent Fourier expansion coefficients. Eqn. (2.66) can be inserted for $\langle\psi|X|\psi\rangle$ in eqn. (2.61) to yield

$$\begin{aligned}\frac{\mathrm{d}\{Q(t)\}_T}{\mathrm{d}\epsilon_x(\omega)} &= \langle X\rangle + \sum_{y}\sum_{k_1} \langle\langle X;Y\rangle\rangle_{\omega_{k_1}} \epsilon_y(\omega_{k_1})\delta(\omega+\omega_{k_1}) \\ &+ \frac{1}{2}\sum_{y,z}\sum_{k_1,k_2} \langle\langle X;Y,Z\rangle\rangle_{\omega_{k_1},\omega_{k_2}} \epsilon_y(\omega_{k_1})\epsilon_z(\omega_{k_2})\delta(\omega+\omega_{k_1}+\omega_{k_2}) + \ldots ,\end{aligned} \tag{2.67}$$

which connects the quasienergy to the response functions. In eqn. (2.67), $\delta(\omega)$ is defined to be zero, unless $\omega = 0$, in which case it is unity. Finally, the structure of eqn. (2.67) can be recognized to be that of a perturbation expansion, where the response functions take the place of the derivatives of the quasienergy. From this, we can write down the quasienergy derivative

$$\langle X\rangle = \frac{\mathrm{d}\{Q(t)\}_T}{\mathrm{d}\epsilon_x(0)} \tag{2.68}$$

and the response functions

$$\langle\langle X;Y\rangle\rangle_{\omega_{k_1}} = \frac{\mathrm{d}^2\{Q(t)\}_T}{\mathrm{d}\epsilon_x(\omega_0)\mathrm{d}\epsilon_y(\omega_{k_1})};\omega_0 = -\omega_{k_1}, \tag{2.69}$$

$$\langle\langle X;Y,Z\rangle\rangle_{\omega_{k_1},\omega_{k_2}} = \frac{\mathrm{d}^3\{Q(t)\}_T}{\mathrm{d}\epsilon_x(\omega_0)\mathrm{d}\epsilon_y(\omega_{k_1})\mathrm{d}\epsilon_z(\omega_{k_2})};\omega_0 = -(\omega_{k_1}+\omega_{k_2}), \tag{2.70}$$

and, in general,

$$\langle\langle X;Y,Z\ldots\rangle\rangle_{\omega_{k_1},\omega_{k_2},\ldots} = \frac{\mathrm{d}^{n+1}\{Q(t)\}_T}{\mathrm{d}\epsilon_x(\omega_0)\mathrm{d}\epsilon_y(\omega_{k_1})\mathrm{d}\epsilon_z(\omega_{k_2})\cdots};\omega_0 = -\sum_{j=1}^{n}\omega_{k_j}. \tag{2.71}$$

In this formulation of response theory, the wavefunction perturbed to order n can be used to calculate response properties to order $n+1$, as will be shown in some more detail in Section 2.2.3. Hence, we say that response properties calculated in this way follow the $n+1$ rule. However, using the method of Lagrangian multipliers, it is possible to formulate response functions in such a way that the wavefunction to order n can be used to calculate properties up to order $2n+1$. The theory for this method will not be covered here, but will be presented in a density-matrix formulation in Paper I.

2.2.3 Molecular properties

The previous section dealt with obtaining response functions as quasienergy derivatives, and in this section, the attention will be shifted to the molecular properties that these response functions describe.

There is a vast number of properties that might be of interest to the researcher, but this and later sections will only deal with properties related to the electric dipole of a system when subjected to one or more electric fields and properties that stem from shifting the molecule's nuclei, and to some extent properties that combine these two categories, since these categories together encompass well the properties that have been explored in the papers of this thesis.

When the molecular system is subjected to an electromagnetic field, where $\mathbf{F}$, $\mathbf{G}$, and $\mathbf{B}$ are the electric field, electric field gradient and magnetic field, respectively, the potential $\hat{V}^t$ can be written as[20]

$$\hat{V}^t = -\mathbf{F}\cdot\hat{\mu} - \mathbf{G}\cdot\hat{\mathbf{\Theta}} - \mathbf{B}\cdot\hat{\mathbf{m}} - \text{higher order terms}, \tag{2.72}$$

where, using the atomic masses, charges and positions m_p, q_p, and $\mathbf{r}_p$, we have introduced the electric dipole operator

$$\hat{\mu} = \sum_p q_p \mathbf{r}_p, \tag{2.73}$$

the electric quadrupole operator

$$\hat{\mathbf{\Theta}} = \sum_p \frac{q_p}{2} \mathbf{r}_p \mathbf{r}_p^T, \tag{2.74}$$

and the magnetic dipole operator

$$\hat{\mathbf{m}} = \sum_p \frac{q_p}{2m_p} \mathbf{l}_p = \sum_p \frac{q_p}{2m_p} \mathbf{r}_p \times \nabla_p, \tag{2.75}$$

where $\hat{\mathbf{\Theta}}$ is a symmetric 3×3 matrix. These contributions to $\hat{V}^t$ all come from a multipole expansion of the electromagnetic wave vector, and this expansion can be extended to include higher-order terms. However, in this work, we are primarily concerned with effects involving the electric dipole operator, and we will make the approximation where eqn. (2.72) is truncated after the $-\mathbf{F} \cdot \hat{\mu}$ term, so that

$$\hat{V}^t = -\mathbf{F} \cdot \hat{\mu}. \tag{2.76}$$

We note that this approximation is sufficient for a large number of computational tasks, and that in many cases, the vast majority of the effect of a perturbing electric field is adequately described with this truncation. The electric field takes the form

$$\mathbf{F} = f e^{-i\omega t} + \left(f e^{-i\omega t} \right)^*, \tag{2.77}$$

where the Jones vector f was introduced [21]. This vector describes the amplitude, phase and polarization of the electric field. The effect on the system of applying an electric field can be described by perturbations to the quasienergy as

$$Q = E_0 + f Q^f + f^* Q^{f^*} + \frac{1}{2} f f Q^{ff} + f^* f Q^{f^* f} + \frac{1}{2} f^* f^* Q^{f^* f^*} + \ldots. \tag{2.78}$$

In eqn. (2.78), a superscript on Q denotes differentiation as in eqns. (2.69)-(2.71). Looking at the properties in this expansion, it is seen, in line with eqn. (2.61), that the first derivative Q^f is

$$Q^f = \frac{\mathrm{d}\{Q(t)\}_T}{\mathrm{d}f(\omega)} = \{-\langle\psi|\hat{\mu}|\psi\rangle e^{-i\omega t}\}_T. \tag{2.79}$$

We note that eqn. (2.79) contains only the zeroth-order wavefunction $|\psi\rangle$, which is in line with the discussion of the $n+1$ rule made in the previous section. Turning now to the higher-order derivatives Q^{ff}, Q^{f^*f}, and $Q^{f^*f^*}$, we consider only the cases where the perturbing field has a frequency $\omega \neq 0$. It is then seen that $Q^{ff} = 0$ and $Q^{f^*f^*} = 0$ because of the requirement $\omega_0 = -\omega_{k_1}$ in eqn. (2.69). However, Q^{f^*f} can be nonzero and will be explored in the following. Taking the derivative with respect to f^* of eqn. (2.79), the expression

$$\begin{aligned} Q^{ff^*} = \frac{\mathrm{d}^2\{Q(t)\}_T}{\mathrm{d}f(\omega)\mathrm{d}f^*(-\omega)} &= \frac{\mathrm{d}}{\mathrm{d}f^*(-\omega)}\{-\langle\psi|\hat{\mu}|\psi\rangle e^{-i\omega t}\}_T \\ &= \{-\left(\langle\psi^f|\hat{\mu}|\psi\rangle e^{-i\omega t} + \langle\psi|\hat{\mu}|\psi^{f^*}\rangle e^{-i\omega t}\right)\}_T \end{aligned} \tag{2.80}$$

is found, and it is seen that it is necessary to calculate the first-order perturbed wavefunction ψ^f in order to determine Q^{ff^*}. Differentiating eqn. (2.37), where we let it be implicit that we also evaluate the resulting expression at zero field strength, we see that

$$\begin{gathered} \frac{\mathrm{d}}{\mathrm{d}f}\left(\hat{H} + \hat{V}^t - i\frac{\partial}{\partial t} - Q\right)|\psi\rangle = 0 \\ \downarrow \\ \left(\hat{H} + \hat{V}^t - i\frac{\partial}{\partial t} - Q\right)|\psi^f\rangle = \left(e^{-i\omega t}\hat{\mu} + Q^f\right)|\psi\rangle, \\ \downarrow \\ \left(\hat{H} - \omega - E_0\right)|\psi^f\rangle = \left(e^{-i\omega t}\hat{\mu}\right)|\psi\rangle, \end{gathered} \tag{2.81}$$

where it was used that $Q^f = 0$ unless $\omega = 0$, and where the evaluation at zero field strength means that $\hat{V}^t = 0$ and that Q is the unperturbed ground-state energy E_0. Furthermore, the only time-dependent term on the right-hand side of the second line of eqn. (2.81) is $e^{-i\omega t}$, whereas the only time-dependent term on the corresponding left-hand side is $|\psi^f\rangle$, so $|\psi^f\rangle$ must have the phase factor $e^{-i\omega t}$. Consequently, $-i\frac{\partial}{\partial t}|\psi^f\rangle = \omega|\psi^f\rangle$, and this is used when going from the second to the third line of eqn. (2.81).

Let the ground state be denoted by $|\psi_0\rangle$ and an excited eigenstate of $\hat{H}$ by $|\psi_x\rangle$, so that all the states make up a complete orthonormal basis. Then, $\hat{H}$ can be written as

$$\hat{H} = E_0|\psi_0\rangle\langle\psi_0| + \sum_{x\neq 0} E_x|\psi_x\rangle\langle\psi_x|, \tag{2.82}$$

so that, by the resolution of the identity, $|\psi_0\rangle\langle\psi_0| + \sum_x |\psi_x\rangle\langle\psi_x| = 1$. By the same principle, we can write the inverse of $\left(\hat{H} - \omega - E_0\right)$ as

$$\left(\hat{H} - \omega - E_0\right)^{-1} = \frac{1}{E_0 - \omega - E_0}|\psi_0\rangle\langle\psi_0| + \frac{1}{E_x - \omega - E_0}|\psi_x\rangle\langle\psi_x|. \tag{2.83}$$

Inserting eqn. (2.83) into eqn. (2.81), the first-order perturbed wavefunction $|\psi^f\rangle$ can now be written as

$$|\psi^f\rangle = e^{-i\omega t}\left(-\frac{\langle\psi_0|\hat{\mu}|\psi_0\rangle}{\omega}|\psi_0\rangle + \sum_x \frac{\langle\psi_x|\hat{\mu}|\psi_0\rangle}{E_x - \omega - E_0}|\psi_x\rangle\right). \tag{2.84}$$

A similar derivation for $|\psi^{f^*}\rangle$ would show that it could be obtained by changing ω to $-\omega$ in eqn. (2.84). Finally, inserting ψ^f and ψ^{f^*} into eqn. (2.80), the expression

$$Q^{ff^*} = -\sum_x \left[\frac{\langle\psi_0|\hat{\mu}|\psi_x\rangle\langle\psi_x|\hat{\mu}|\psi_0\rangle}{(E_x - E_0) + \omega} + \frac{\langle\psi_0|\hat{\mu}|\psi_x\rangle\langle\psi_x|\hat{\mu}|\psi_0\rangle}{(E_x - E_0) - \omega}\right] \tag{2.85}$$

is found, expressing Q^{ff^*} as a sum over excited states of the system. Furthermore, noting that the electric dipole moment can be expanded in a Taylor expansion as

$$\mu = \mu^0 + \alpha f + \frac{1}{2}\beta ff + \frac{1}{6}\gamma fff + \ldots, \tag{2.86}$$

where μ^0 is the dipole moment in the absence of external fields, and where we introduced the molecular polarizability and first and second hyperpolarizabilities α, β, and γ, respectively, it can be recognized that Q^{ff^*} corresponds to the negative of the molecular polarizability in eqn. (2.86). We note that although the derivation leading to eqn. (2.85) was done under the assumption that $\omega \neq 0$, we will use it in Section 2.3.3 for the case $\omega = 0$. In general, higher-order quasienergy derivatives with respect to electric fields

correspond to higher-order terms in eqn. (2.86). To represent the general high-order case, we introduce a notation where electric dipole perturbation differentiation is represented by a superscript F on Q, and the subscripts on the differentiated Q denote, in order, the frequencies of the associated perturbation. For example, the second hyperpolarizability $\gamma(-2\omega;\omega,\omega,0)$ is represented as $Q^{FFFF}_{-2\omega,\omega,\omega,0}$.

The other kind of perturbation featured in this section is the so-called geometrical perturbation, which comes from displacing the molecule's nuclei. The frequency of such a perturbation is zero, and we denote the perturbation by G. In the quasienergy-derivative notation introduced above, we omit the frequency subscript for G derivatives because it is not needed. The geometrical perturbation is mainly relevant for situations involving molecular vibrations, to be treated in more detail in Section 2.3.

We can expand the energy in the coordinates $\{x_i\}$ of the system as

$$E = E^0 + \sum_i \frac{\partial E}{\partial x_i} x_i + \frac{1}{2!} \sum_{i,j} \frac{\partial^2 E}{\partial x_i \partial x_j} x_i x_j + \frac{1}{3!} \sum_{i,j,k} \frac{\partial^3 E}{\partial x_i \partial x_j \partial x_k} x_i x_j x_k + \frac{1}{4!} \sum_{i,j,k,l} \frac{\partial^4 E}{\partial x_i \partial x_j \partial x_k \partial x_l} x_i x_j x_k x_l + \ldots, \tag{2.87}$$

where the type of coordinates used is unspecified. Typically, the expansion is done with respect to either the Cartesian or the normal coordinates of the system. The latter will be presented in Section 2.3. From eqn. (2.87), we can recognize elements of the molecular gradient $\frac{\partial E}{\partial x_i}$, the Hessian $\frac{\partial^2 E}{\partial x_i \partial x_j}$, and the cubic and quartic force fields $\frac{\partial^3 E}{\partial x_i \partial x_j \partial x_k}$ and $\frac{\partial^4 E}{\partial x_i \partial x_j \partial x_k \partial x_l}$, respectively. These properties can be expressed in terms of energy derivatives as Q^G, Q^{GG}, Q^{GGG}, and Q^{GGGG}, respectively. We note that these properties can be calculated through the $(n+1)$ rule response formalism introduced earlier, but for high-order properties, one will typically resort to calculations by other rule choices than the $(n+1)$ rule to save computation time. There are several uses for these properties, of which we can mention optimization of the molecular geometry through the Newton method or quasi-Newton methods using the molecular gradient (and additionally the Hessian for the former), determination of the system's normal coordinates (in the so-called harmonic approximation) using the Hessian, and methods to make corrections to various properties to account for the anharmonic nature of molecular vibrations, using various higher-order geometrical derivatives.

Finally, we mention that there exist many well-known combined geometrical and electric dipole properties. This category of properties finds its use in a variety of spectroscopies involving molecular vibrations, and any discussion of these properties is best done after having covered this topic in some more detail. We therefore postpone comments about combined electric and geometric properties to a later part of Section 2.3.

2.3 Molecular vibrations

In this section, we present some topics related to molecular vibrations. We begin by showing how vibrations in a molecule can be identified and characterized, and then discuss some more advanced topics like corrections of fundamental vibrational frequencies by high-order force constants and vibrational contributions to polarization properties. Finally, we make some remarks related to vibrational spectroscopies.

2.3.1 Identifying molecular vibrations

As shown in eqn. (2.87), the energy can be expanded in the geometrical coordinates of the system. We will in the following always assume that the molecule is at its equilibrium geometry, so that the gradient $\mathbf{g} = \nabla E = [\partial E/\partial x_1, \partial E/\partial x_2, \ldots, \partial E/\partial x_M]^T$ is zero, where M is the number of coordinates.

The starting point for the discussion of molecular vibrations is the molecular Hessian $\mathbf{H}$. As mentioned earlier, the Hessian is the matrix containing the second derivatives of the molecular energy with respect to some kind of geometrical displacement. A typical choice of displacement coordinate is the Cartesian coordinates X_i of the atoms in the molecule, so that, for a molecule with N atoms, we define the Cartesian Hessian $\mathbf{H}_{\text{cart}}$ as

$$\mathbf{H}_{\text{cart}} = \begin{pmatrix} \frac{\partial^2 E}{\partial X_1^2} & \frac{\partial^2 E}{\partial X_1 \partial X_2} & \cdots & \frac{\partial^2 E}{\partial X_1 \partial X_{3N}} \\ \frac{\partial^2 E}{\partial X_2 \partial X_1} & \frac{\partial^2 E}{\partial X_2^2} & \cdots & \frac{\partial^2 E}{\partial X_2 \partial X_{3N}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 E}{\partial X_{3N} \partial X_1} & \frac{\partial^2 E}{\partial X_{3N} \partial X_2} & \cdots & \frac{\partial^2 E}{\partial X_{3N}^2} \end{pmatrix}. \tag{2.88}$$

The molecule can vibrate in certain different ways that can be expressed as displacements of any of the Cartesian coordinates of its constituent atoms. We define a normal mode as such a way in which a molecule can vibrate. A well-established assumption, adopted here, is that the oscillations of the

vibrational modes are simple harmonic oscillations. All of the information about the molecular vibrations is then contained in $\mathbf{H}_{\text{cart}}$. In this approximation, the normal modes vibrate independently of each other.

The vibrational modes will be independent of the location or orientation of the molecule in space, so that translational and rotational degrees of freedom should be eliminated. For nonlinear molecules, there are six such degrees of freedom, whereas for linear molecules, there are five.

The molecule is defined by $3N$ Cartesian coordinates, but this is an overdefinition. The extent of the overdefinition is the number of the translational and rotational degrees of freedom, and so, there are $3N-6$ or $3N-5$ independent normal modes for nonlinear and linear molecules, respectively.

The normal modes and their corresponding frequencies of vibration can be identified by an eigenanalysis of $\mathbf{H}_{\text{cart}}$. This is under the assumptions that translational and rotational degrees of freedom have been projected out of $\mathbf{H}_{\text{cart}}$ (but at the equilibrium geometry, these effects will be small, so such a projection is usually not necessary), and that the elements of $\mathbf{H}_{\text{cart}}$ have been weighted according to the masses of the nuclei that are related to each element, yielding the mass-weighted, translation/rotation-invariant Cartesian Hessian $\mathbf{H}_{\text{cart, mw}^{\text{proj}}}$. The procedures for such projection and mass-weighting will not be covered here, but it is remarked that they are straightforward and readily carried out by a computer program.

Upon diagonalization of $\mathbf{H}_{\text{cart, mw}^{\text{proj}}}$, a set of $3N$ eigenvalues λ and a $3N \times 3N$ eigenvector matrix $\mathbf{Q}$ will be found. There will be six eigenvalues of value zero (or five for a linear molecule). Disregarding the zero eigenvalues of λ and removing the corresponding columns of $\mathbf{Q}$, the remaining part of $\mathbf{Q}$ is a $3N \times (3N-6)$ (or $3N \times (3N-5)$) matrix defining the normal modes in terms of Cartesian displacements, and for each of the eigenvalues λ_i, the frequency ω_i of the corresponding normal mode Q_i is given by $\omega_i = \sqrt{\lambda_i}$. For reference, we can now write eqn. (2.87) as

$$E = E^0 + \sum_a \frac{\partial E}{\partial Q_a} Q_a + \frac{1}{2!} \sum_{a,b} \frac{\partial^2 E}{\partial Q_a \partial Q_b} Q_a Q_b + \frac{1}{3!} \sum_{a,b,c} \frac{\partial^3 E}{\partial Q_a \partial Q_b \partial Q_c} Q_a Q_b Q_c + \frac{1}{4!} \sum_{a,b,c,d} \frac{\partial^4 E}{\partial Q_a \partial Q_b \partial Q_c \partial Q_d} Q_a Q_b Q_c Q_d + \ldots, \tag{2.89}$$

where the expansion is now with respect to normal modes. Finally, we note that it is also possible to transform these normal coordinates to so-called reduced[22] normal coordinates q, where

$$q_i = \sqrt{\frac{2\pi c\omega_i}{\hbar}} Q_i \tag{2.90}$$

for some normal mode i, where q_i is typically expressed in units of wavenumbers (cm^{-1}). Reduced normal modes are often used in various applications because it simplifies expressions involving vibrational matrix elements.

2.3.2 Corrections to vibrational frequencies

The assumption that the normal mode vibrations behave as harmonic oscillators, called the harmonic approximation, is a good approximation, but in general, there are situations where such a description is not adequate. In order to deal with this, eqn. (2.89) can be truncated at higher orders than the second-order truncation used in the harmonic approximation, and corrections to the harmonic frequencies ω_i can be carried out by the application of perturbation theory, yielding a corrected set of fundamental frequencies ν_i. A common procedure is to use second-order perturbation theory, which entails truncating eqn. (2.89) after the fourth-order (quartic) terms and also including some rotational effects. By this procedure, using reduced normal coordinates, the corrected fundamental frequencies ν_i are given by the expressions[23, 24, 25]

$$\nu_i = \omega_i + 2X_{ii} + \sum j \neq i \frac{X_{ij}}{2}, \tag{2.91}$$

where

$$X_{ii} = \frac{\phi_{iiii}}{16} - \sum_k \frac{\phi_{iik}^2 \left(8\omega_i^2 - 3\omega_k^2\right)}{16\omega_k \left(4\omega_i^2 - \omega_k^2\right)} \tag{2.92}$$

and

$$X_{ij} = \frac{\phi_{iijj}}{4} - \sum_k \frac{\phi_{iik}\phi_{jjk}}{4\omega_k} - \sum_k \phi_{ijk}^2 \frac{\omega_k \left(\omega_i^2 + \omega_j^2 - \omega_k^2\right)}{2\Omega_{ijk}} + \sum_\alpha B_\alpha (\zeta_{ij}^\alpha)^2 \left(\frac{\omega_i}{\omega_j + \omega_j}\omega_i\right), \tag{2.93}$$

where ϕ_{ijk} and ϕ_{ijkl} are cubic and quartic force constants, respectively, B_α is a rotational constant for the Cartesian axis α, ζ_{ij}^α is a Coriolis coupling tensor element describing vibration-rotation coupling, while

$$\Omega_{ijk} = (\omega_i + \omega_j + \omega_k)\left(-\omega_i + \omega_j + \omega_k\right)\left(\omega_i - \omega_j + \omega_k\right)\left(\omega_i + \omega_j - \omega_k\right). \tag{2.94}$$

A complication of this procedure is the fact that some differences between overtones $2\omega_i$ or combination frequencies $\omega_i + \omega_j$ $(i \neq j)$ can be very close to fundamental harmonic frequencies ω_k, so that the perturbation theory breaks down because denominators in eqns. (2.92) and (2.93) approach zero. This phenomenon is called a Fermi resonance, and methods to deal with this have been developed, but will not be covered here.

2.3.3 Vibrational contributions to molecular properties

In this section, we develop expressions for vibrational contributions to the molecular polarizability and first hyperpolarizability. The theory presented here follows the work of Bishop, Kirtman, and Luis[39, 40, 41].

In Section 2.2.3, the calculation of the molecular polarizability α was presented. This property can be written in a sum-over-states formulation as

$$\alpha_{\alpha\beta}(-\omega_\sigma;\omega_1) = \sum_{\bar{m}>0}\left[\frac{\langle\psi_0|\hat{\mu_\alpha}|\psi_{\bar{m}}\rangle\langle\psi_{\bar{m}}|\hat{\mu_\beta}|\psi_0\rangle}{(E_{\bar{m}}-E_0)-\omega_\sigma} + \frac{\langle\psi_0|\hat{\mu_\beta}|\psi_{\bar{m}}\rangle\langle\psi_{\bar{m}}|\hat{\mu_\alpha}|\psi_0\rangle}{(E_{\bar{m}}-E_0)+\omega_1}\right], \tag{2.95}$$

where Greek subscripts on polarization properties represent Cartesian axes, and where ω_σ is the sum of all incident frequencies so that, here, $\omega_\sigma = \sum_i \omega_i = \omega_1$. In eqn. (2.95), the excited state characterized by the quantum number $\bar{m}$ is in general taken to involve both the electronic, vibrational and rotational states of the system. In the following, as an approximation, the rotational states will be disregarded, except for the extent to which they can later be taken into consideration by orientational averaging. The attention will instead be given to the electronic and vibrational states. The quantum number $\bar{m}$ then refers to a vibronic state $|\psi_{\bar{m}}\rangle \equiv |\bar{m}\rangle$, which is a combined electronic and vibrational state of the system.

Denoting the quantum numbers of the electronic and vibrational states of the system by M and m, respectively, it is, by employing the Born-Oppenheimer approximation, possible to separate a summation over the vibronic $\bar{m}$ into electronic and vibrational parts. By considering terms involving the electronic or vibrational ground states separately, the state summation over the excited $\bar{m}$ can be written as

$$\sum_{\bar{m}>0} = \sum_{m>0}\Big|_{M=0} + \sum_m \sum_{M>0}. \tag{2.96}$$

Applying the summation splitting in eqn. (2.96) to the state summation in eqn. (2.95), two distinct contributions to $\alpha_{\alpha\beta}$ can be identified, each corre-

sponding to one term on the right-hand side of eqn. (2.96). The contribution corresponding to the first of these terms is called the pure vibrational (PV) term, while the final term is a combination of the zero-point vibrational average (ZPVA) and electronic contribution to the property. When using the response theory of Section 2.2, typically only the electronic contribution to the property is calculated. This is usually the largest contribution to the property, but the PV and ZPVA contributions can also be important. Disregarding the ZPVA contribution as it is outside the scope of this work, we will in the following show how working expressions for the PV contributions can be derived. We will therefore only concern ourselves with the term $\sum_{m>0}\big|_{M=0}$.

Starting with eqn. (2.95), the summation splitting means that $|\bar{m}\rangle = |M, m\rangle = |0, m\rangle$, so that

$$\begin{aligned}\alpha^{PV}_{\alpha\beta}(-\omega_\sigma;\omega_1) &= \sum_{m>0}\sum P_{\alpha\beta}\left[\frac{\langle 0,0|\hat{\mu_\alpha}|0,m\rangle\langle 0,m|\hat{\mu_\beta}|0,0\rangle}{\omega_m-\omega_\sigma}\right] \\ &= \sum_{m>0}\sum P_{\alpha\beta}\left[\frac{\langle 0|\mu_\alpha|m\rangle\langle m|\mu_\beta|0\rangle}{\omega_m-\omega_\sigma}\right],\end{aligned} \tag{2.97}$$

where ω_m denotes the energy of the vibrational state $|m\rangle$ relative to the ground state and the perturbation sum operator $\sum P_{\alpha\beta}$ carries out the simultaneous permutation of the pairs $(\alpha, -\omega_\sigma)$ and (β, ω_1) of associated axes and frequencies and sums the terms thus obtained. When going from the first to the second line of eqn. (2.97), the integration $\langle 0|\hat{\mu}_\alpha|0\rangle \equiv \mu_\alpha$ was done, where the state in the bra and ket is the electronic ground state.

As was done for the energy, the electric dipole moment can also be expanded in the normal coordinates of the system. Let P be a polarization property. Then, the expansion

$$P = P^0 + \sum_a \frac{\partial P}{\partial Q_a}Q_a + \frac{1}{2!}\sum_{a,b}\frac{\partial^2 P}{\partial Q_a \partial Q_b}Q_aQ_b + \frac{1}{3!}\sum_{a,b,c}\frac{\partial^3 P}{\partial Q_a\partial Q_b\partial Q_c}Q_aQ_bQ_c + \ldots \tag{2.98}$$

can be made. The twofold approximation where eqn. (2.98) is truncated after the first derivative, and where the harmonic approximation is made for the vibrational wavefunction, is called the double harmonic approximation, and this is adopted in the following. Inserting the appropriately truncated expansion of eqn. (2.98) into eqn. (2.97), we get

$$\alpha^{PV}_{\alpha\beta}(-\omega;\omega) = \sum_{m>0}\sum P_{\alpha\beta}\left[\frac{\langle 0|\mu^0_\alpha + \sum_a \frac{\partial\mu_\alpha}{\partial Q_a}Q_a|m\rangle\langle m|\mu^0_\beta + \sum_b \frac{\partial\mu_\beta}{\partial Q_b}Q_b|0\rangle}{\omega_m - \omega}\right]$$
$$= \sum_{m>0}\sum P_{\alpha\beta}\sum_{a,b}\left[\frac{\partial\mu_\alpha}{\partial Q_a}\frac{\partial\mu_\beta}{\partial Q_b}\frac{\langle 0|Q_a|m\rangle\langle m|Q_b|0\rangle}{\omega_m - \omega}\right], \tag{2.99}$$

where the terms involving μ^0_α and μ^0_β vanish because they involve products $\langle 0|m\rangle$, which are zero by orthonormality. When going from the first to the second line of eqn. (2.99), it was also used that $\frac{\partial\mu_\alpha}{\partial Q_a}$ and $\frac{\partial\mu_\beta}{\partial Q_b}$ are scalars and can therefore be moved outside the integral brackets. The vibrational state $|m\rangle$ can be said to consist of individual wavefunctions k of each normal mode with quantum number m_k, so that $|m\rangle = |a_{m_a}b_{m_b}\cdots N_{m_N}\rangle$, where N is here used both to denote the number of normal modes of the system and the wavefunction of the Nth normal mode. Each of these wavefunctions contain Hermite polynomials, which have the property that [26]

$$\langle a_{m_a}|Q_a|a_{m_a\pm1}\rangle = \sqrt{\frac{m_a + \frac{1}{2} \pm \frac{1}{2}}{2\omega_a}}, \tag{2.100}$$

and the integral is zero unless the bra and ket quantum number differ by exactly one. Applying eqn. (2.100) to the term $\langle 0|Q_a|m\rangle$ in eqn. (2.99), it is seen that this term can only be nonzero if $|m\rangle = |a_1b_0\cdots N_0\rangle$, i.e. the state corresponding to the first excited state of one of the vibrational modes. Denoting this state by $|a\rangle$, and inserting in eqn. (2.99), the expression

$$\alpha^{PV}_{\alpha\beta}(-\omega;\omega) = \frac{1}{2}\sum P_{\alpha\beta}\sum_a \frac{\frac{\partial\mu_\alpha}{\partial Q_a}\frac{\partial\mu_\beta}{\partial Q_a}}{\omega_a^2 - \omega^2} \tag{2.101}$$

is found, where a similar argument to the one above was used to find that $b = a$, and the summations over m and b are no longer necessary. The frequency ω_a refers to the energy of the state $|a\rangle$ relative to the ground state.

The corresponding PV contribution to the first hyperpolarizability $\beta_{\alpha\beta\gamma}$ can be derived from the same principles, but the derivation is somewhat more involved. Using a form analogous to eqn. (2.97), but for the moment still considering all vibronic states, $\beta_{\alpha\beta\gamma}$ can be written as

$$\beta^{PV}_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2) = \sum_{\bar{m}>0}\sum_{\bar{n}>0}\sum P_{\alpha\beta\gamma}\left[\frac{\langle 0|\hat{\mu_\alpha}|\bar{m}\rangle\langle\bar{m}|\bar{\hat{\mu}_\beta}|\bar{n}\rangle\langle\bar{n}|\hat{\mu_\gamma}|0\rangle}{(\omega_{\bar{m}}-\omega_\sigma)(\omega_{\bar{n}}-\omega_2)}\right], \tag{2.102}$$

where $\bar{\hat{\mu}_\beta} = \hat{\mu_\beta} - \langle 0|\hat{\mu_\beta}|0\rangle$, where the integration was done over electronic states. The vibronic state summations can now be split in the same way as was done in eqn. (2.96), but now, this splitting produces four contributions, namely

$$\sum_{\bar{m}>0}\sum_{\bar{n}>0} = \sum_{m,n>0}\Bigg|_{M,N=0} + \sum_{m}\sum_{M>0}\sum_{n>0}\Bigg|_{N=0} + \sum_{m>0}\sum_{n}\sum_{N>0}\Bigg|_{M=0} + \sum_{m,n}\sum_{M,N>0}, \tag{2.103}$$

where the ZPVA and electronic contributions are contained in the last term. The PV contribution $\beta^{PV}_{\alpha\beta\gamma}$ can be written as as sum of two contributions as

$$\beta_{\alpha\beta\gamma} = [\mu\alpha] + [\mu^3], \tag{2.104}$$

where $[\mu^3]$ corresponds to the part of eqn. (2.102) that includes only contributions from the first term on the right-hand side of eqn. (2.103). The contribution $[\mu\alpha]$ contains the corresponding contributions from the second and third right-hand side terms of eqn. (2.103). Adopting the double harmonic approximation, the contribution $[\mu^3]$ will be zero due to the Hermite integral properties of eqn. (2.100). To see this, it is sufficient to consider the term

$$\sum_{m,n>0}\sum_{a,b,c}\langle 0|Q_a|m\rangle\langle m|Q_b|n\rangle\langle n|Q_c|0\rangle, \tag{2.105}$$

which is proportional to the $[\mu^3]$ term after the appropriate Taylor expansions have been made in the double harmonic approximation. In this expression, it is clear that $|m\rangle$ must be $|a_1\rangle$. From this, the state $|n\rangle$ must be $|a_2\rangle$ or $|a_1b_1\rangle$ where $b \neq a$, since $|n\rangle$ cannot be the ground state. However, the last integral $\langle n|Q_c|0\rangle$ must be zero since the bra and ket states differ by two quantum numbers (either two quanta for one normal mode or one for each of two different modes), and the entire $[\mu^3]$ contribution must therefore be zero.

Turning now to $[\mu\alpha]$, this term can be written as

$$[\mu\alpha] = \sum_{M>0}\sum_{m}\sum_{n>0}\sum P_{\alpha\beta\gamma}\left[\frac{\langle 0,0|\hat{\mu_\alpha}|M,m\rangle\langle M,m|\bar{\hat{\mu}}_\beta|0,n\rangle\langle 0,n|\hat{\mu_\gamma}|0,0\rangle}{(\omega_{M,m}-\omega_\sigma)(\omega_n-\omega_2)}\right] + \sum_{m>0}\sum_{N>0}\sum_{n}\sum P_{\alpha\beta\gamma}\left[\frac{\langle 0,0|\hat{\mu_\alpha}|0,m\rangle\langle 0,m|\bar{\hat{\mu}}_\beta|N,n\rangle\langle N,n|\hat{\mu_\gamma}|0,0\rangle}{(\omega_m-\omega_\sigma)(\omega_{N,n}-\omega_2)}\right] \tag{2.106}$$

where $\omega_{M,m}$ is the energy of the vibronic state $|M,m\rangle$ relative to the ground state. Making the approximation $\omega_{M,m} \approx \omega_{M,0} \equiv \omega_M$ (and similarly for $\omega_{N,n}$), resolution of the identity can be applied over the vibrational states $|m\rangle$ and $|n\rangle$ of the first and second terms of the right-hand side of eqn. (2.106), respectively, since there now are no other places referring to those states in these terms than the products $|m\rangle\langle m|$ and $|n\rangle\langle n|$, respectively. Furthermore, the sum-over-states expression of eqn. (2.95) for the polarizability $\alpha(0;0)$ can be recognized in the resulting expressions after renaming of states and making use of the permutational symmetry afforded by the summation $\sum P_{\alpha,\beta,\gamma}$. Applying the double-harmonic approximation, rewriting eqn. (2.106) in terms of the polarizabilities that were recognized and simplifying the resulting expresssion, the PV contribution to $\beta_{\alpha\beta\gamma}$ in the double harmonic approximation can be written as

$$\beta^{PV}_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2) = [\mu\alpha] = \frac{1}{2}\sum P_{\alpha\beta\gamma}\sum_a \frac{\frac{\partial\mu_\alpha}{\partial Q_a}\frac{\partial\alpha_{\beta\gamma}}{\partial Q_a}}{\omega_a^2-\omega_\sigma^2}. \tag{2.107}$$

Corresponding derivations can be done for higher-order polarization properties, but we will not concern ourselves with this here.

Finally, we note that it is possible to go beyond the double-harmonic approximation. Including higher-order terms in the expansions of eqns. (2.98) and (2.89) is called introducing electrical and mechanical anharmonicity, respectively. The derivations of such higher-order contributions are complicated and not suitable to present in this text, but we remark that for their evaluation, it is necessary to be able to calculate higher-order geometrical derivatives of polarization properties.

2.3.4 Vibrational spectroscopies and geometrical derivatives of polarization properties

In the final part of this section, we will make some remarks related to spectroscopies involving molecular vibrations. When a system is subjected to an

electric field or several fields with frequencies in the infrared (IR) domain, it can be excited to a higher vibrational state. This can also happen indirectly from inelastic scattering by the application of an electric field or fields in the ultraviolet or visible range, as in Raman spectroscopy. If the Born-Oppenheimer approximation is adopted, the intensity of the observed signal in these spectroscopies is typically proportional to an integral $\langle 0|Q_a|m\rangle$, where $|m\rangle$ is a vibrational state, or proportional to a series of integrals like in eqn. (2.105). Therefore, derivations with similarities to the ones leading up to eqns. (2.101) and (2.107), using the expansions of eqns. (2.98) and (2.89), can typically be done to obtain expressions for the spectroscopic intensities. We will not cover these derivations in detail, but we mention that in the double-harmonic approximation, assuming that the intensities can be derived in the way just mentioned, the intensity associated with a transition to a singly excited state $|a_1\rangle$ can only be nonzero if a corresponding first geometrical derivative $\frac{\partial P}{\partial Q_a}$ of the associated polarization property P is nonzero. All other kinds of excited states (such as overtones and combination excited states) will not contribute to a spectrum calculated under this approximation. For IR spectroscopy, the associated property is the dipole moment, and for Raman spectroscopy, it is the polarizability. It is this consideration that gives rise to the well-known selection rules $\frac{\partial \mu}{\partial Q_a} \neq 0$ and $\frac{\partial \alpha}{\partial Q_a} \neq 0$ for IR and Raman transitions, respectively. As was done for the PV contributions, we note again that anharmonicity can be introduced by including higher-order terms in the expansions of eqns. (2.98) and (2.89). By including anharmonicity, higher-order effects can appear, including signals from overtone and combination excitations and Fermi resonance effects. This can give contributions that lead to "weakly allowed" signals in the well-known spectroscopies.

2.4 Programming techniques for a general response code

In this section, we present two of the programming techniques used in the development of the general response code featured in paper I and applied in the subsequent papers: (Circularly) linked lists and recursive programming.

2.4.1 (Circularly) linked lists

Suppose, for a computer program, that a programmer wants to store information that may be in an unwieldy but still a well-defined format. Suppose

furthermore that there may be an indefinite number of such pieces of information, and that it is desirable to be able to freely insert into and delete from storage such pieces as the program is run. Finally, suppose that the speed with which relevant information is located upon inquiry is not crucial. Then, linked lists may be a good option.

To understand linked lists, it is necessary to introduce the concept of a pointer. In computer programs, variables and data structures are typically declared (or their structure is inferred by the compiler), and the relevant space in memory is reserved for the information to be stored in the variable or datatype. A pointer is also declared with respect to a given kind of variable or datatype. However, it does not contain the information of a datatype, but may instead contain information that tells where an instance of such a datatype is stored, i.e. it *points* to such a location. If it does, a pointer is said to be associated. To disassociate a pointer is called to nullify it. When referred to as a regular variable or datatype, the pointer will return the relevant information located at the position in memory to which it is pointing. Because of this, pointers are a flexible tool that can be used to save memory when dealing with information that would otherwise be duplicated, or it can be used to build topological relations between data.

A linked list is a data structure that contains a given number of entries, which are instances of a datatype. In its basic form, this datatype (the entry) contains two parts:

1. A pointer to the next element in the list
2. Information (if any) stored in the entry

When creating the first entry in a linked list, the pointer is typically left unassociated. Alternatively, in a circularly linked list, the pointer of the first entry points to itself. Inserting a new entry into some position in the list entails reassociating the pointer of the preceding entry to the new entry, while associating the pointer of the new entry to where the pointer of the preceding entry was associated before the insertion of the new element (or leaving it disassociated if the preceding entry was the final entry in a non-circularly linked list). An illustration of the structure of a circularly linked list is shown in Figure 2.4.1.

To retrieve information from the list, it is necessary to start at some entry – typically the first entry in a non-circularly linked list, but an arbitrary element is sufficient in a circularly linked list – and then traverse the list by following the pointers of each entry until the desired entry is found (typically, an entry may contain some header information identifying it). Once the

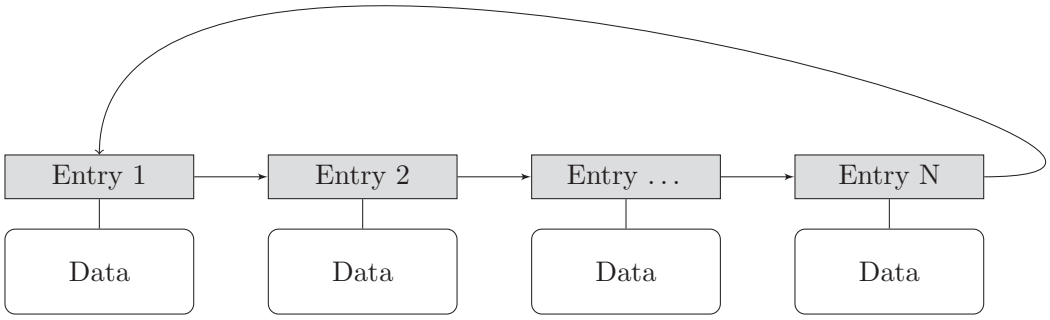

Figure 2.1: Circularly linked list. Pointer associations are shown by arrows.

correct entry is located, the information it contains can be addressed and handled in a regular way.

A drawback of linked lists is that traversal may be time-consuming when the number of entries is large, and each new entry added could in general add to the retrieval time of many or all of the entries. However, the circularly linked list methodology is sufficient for the purposes of this work, and possible ways of addressing situations where retrieval time is more important will therefore not be covered here.

2.4.2 Recursive programming

Another key element of the code that has been developed in this work is the use of recursive programming. Recursive routines can be used to create code that is compact and general in a situation where there is an indefinite number of layers, or orders, of complexity.

A recursive routine is a routine that can invoke itself, usually with different arguments than the ones of its present invocation. An often-used example to illustrate recursive routines is the task of calculating the factorial of a (nonnegative) integer N. An iterative (non-recursive) function is shown in Algorithm 1.

A recursive factorial function can also be constructed and is shown in Algorithm 2.

Algorithm 1 Iterative factorial function

```
fact = 1
for i in 2, N do
    fact = fact · i
end for
return fact
```

Algorithm 2 Recursive factorial function *fact*

```
if N > 1: then
    return N · fact(N - 1)
end if
if N = 1 or N = 0 : then
    return 1
end if
```

As can be seen from the code, in Algorithm 2, the function constructs the factorial of N (if $N > 1$) by invoking itself at smaller values of the argument until terminating when invoked with argument 1, replicating the definition

$$N! = N \cdot (N-1) \cdot (N-2) \cdot \ldots \cdot 2 \cdot 1, \tag{2.108}$$

while in Algorithm 1, the factorial is constructed within one invocation. Arguably, none of algorithms 1 and 2 are significantly better than the other in this simple example, but for more complicated situations, the use of recursive routines can result in a compact code. Consider, for example, the task of differentiating the expression for the molecular energy, $\mathcal{E}(\mathbf{D})$, where the $\mathbf{D}$ in parentheses denotes a functional dependence on the density matrix, with respect to some perturbations $a, b, c, \ldots$, collected in a perturbation tuple b_N. In general, both $\mathcal{E}$ and $\mathbf{D}$ depend on the perturbations, and use must be made of both the product and chain rules of differentiation:

$$\begin{aligned}
\mathcal{E}^{a} =& \mathcal{E}^{0,a} \\
\mathcal{E}^{ab} =& \mathcal{E}^{0,ab} + \boldsymbol{\mathcal{E}}^{1,a}\mathbf{D}^{b} + \boldsymbol{\mathcal{E}}^{1,b}\mathbf{D}^{a} + \boldsymbol{\mathcal{E}}^{1}\mathbf{D}^{ab} + (\boldsymbol{\mathcal{E}}^{2}\mathbf{D}^{a})\mathbf{D}^{b} \\
\mathcal{E}^{abc} =& \mathcal{E}^{0,abc} + \boldsymbol{\mathcal{E}}^{1,ab}\mathbf{D}^{c} + \boldsymbol{\mathcal{E}}^{1,ac}\mathbf{D}^{b} + \boldsymbol{\mathcal{E}}^{1,a}\mathbf{D}^{bc} + (\mathcal{E}^{2,a}\mathbf{D}^{b})\mathbf{D}^{c} + \\
& \boldsymbol{\mathcal{E}}^{1,bc}\mathbf{D}^{a} + \boldsymbol{\mathcal{E}}^{1,b}\mathbf{D}^{ac} + (\mathcal{E}^{2,b}\mathbf{D}^{a})\mathbf{D}^{c} + \boldsymbol{\mathcal{E}}^{1,c}\mathbf{D}^{ab} + \boldsymbol{\mathcal{E}}^{1}\mathbf{D}^{abc} + (\boldsymbol{\mathcal{E}}^{2}\mathbf{D}^{ab})\mathbf{D}^{c} + \\
& (\boldsymbol{\mathcal{E}}^{2,c}\mathbf{D}^{a})\mathbf{D}^{b} + (\boldsymbol{\mathcal{E}}^{2}\mathbf{D}^{ac})\mathbf{D}^{b} + (\boldsymbol{\mathcal{E}}^{2}\mathbf{D}^{a})\mathbf{D}^{bc} + ((\boldsymbol{\mathcal{E}}^{3}\mathbf{D}^{a})\mathbf{D}^{b})\mathbf{D}^{c}
\end{aligned} \tag{2.109}$$

As is apparent from the above expressions, the complexity rises rapidly

at higher orders. Note that in the general case, use will be made of truncation rules such as the $n + 1$ and $2n + 1$ rules of Section 2.2, which may remove some terms, but will at the same time add to the complexity of the task due to the need to decide for each term whether to truncate it because of the rule choice or not. An iterative algorithm for carrying out the differentiation would be complicated, and may be difficult to create without resorting to "order-by-order" methods with different ways of handling each order of differentiation, which could result in code that grows rapidly with the highest order of differentiation supported. Using recursion, however, a routine such as Algorithm 3, adapted from Paper I, can be created. This routine can carry out the differentiation of $\mathcal{E}$ to any order, and does so in a modest number of lines. We also remark that the information in some of the contributions thus identified can be re-used in other contributions. It is therefore possible to store contributions in a cache for later retrieval, and the circularly linked list methodology presented in Section 2.4.1 is well suited to this purpose.

Routines such as the one outlined in Algorithm 3 form the backbone of the open-ended response code OpenRSP featured in this work. The structure of the open-ended response theory developed by Andreas Thorvaldsen and co-workers[2] lends itself well to an implementation where recursive routines are featured heavily, and by this, it is possible to create a general code to manage the calculation of any response property. A more detailed explanation of the most important routines in the OpenRSP code can be found in Paper I.

Algorithm 3 Identify energy contributions (b_N, b_{diff})

Arguments: *Perturbation tuple* b_N, *perturbation tuple, list* b_{diff}
First invocation arguments: b_N for the property under consideration, one empty perturbation tuple in b_{diff}
Perturbation tuple: b^*_N
Perturbation tuple, list: b^*_{diff}

if $N > 0$ **then**
  for i in 1, length(b_{diff}) + 1 **do**
    $b^*_{\text{diff}} \leftarrow b_{\text{diff}}$
    if i = length(b_{diff})+1 **then**
      Extend b^*_{diff} by one tuple
      $b^*_{\text{diff},i} \leftarrow b_{N,1}$
    else
      Add $b_{N,1}$ to $b^*_{\text{diff},i}$
    end if
    $b^*_N \leftarrow b_N$
    Remove $b^*_{N,1}$ from b^*_N
    Call self(b^*_N, b^*_{diff})
  end for
else
  if contribution not retrievable from cache **then**
    if not truncating because of rule choice **then**
      Calculate contribution for b_{diff} and store in cache
    end if
  end if
end if

Chapter 3

Summary of papers

3.1 Paper I: A general open-ended response code

In this paper, we present an implementation of the general open-ended response theory by Andreas Thorvaldsen and co-workers[2]. We show that through the use of recursive routines, a program can be made to calculate any molecular property analytically, as long as the necessary contributions from integral codes are available. Various intermediate contributions can be stored in circularly linked lists and retrieved at later stages of the calculation for convenience and computational savings. We demonstrate the code by presenting results of the analytic calculation of the cubic force field of the second hyperpolarizability of HSOH, which is a seventh-order property of such a complexity that a tailored implementation would have been cumbersome to create.

3.2 Paper II: Cubic and quartic force constants

In this paper, we use the OpenRSP program and recent developments in integral codes [27] [28] [29] [30] [31] and exchange-correlation routines [32] [33] to calculate cubic and quartic force constants for a selection of systems at both Hartree-Fock and DFT levels of theory. We use the cubic and quartic force constants to calculate corrected fundamental vibrational frequencies for methane, ethane, benzene, and aniline. It is seen that correlation effects, while not dominant, regularly show differences in fundamental vibrational frequency corrections of up to $\pm 10\%$ compared to the Hartree-Fock results, and sometimes, even larger differences are produced. For the fundamental vibrational frequencies, the DFT (B3LYP) results show the best agreement

to experimental values.

3.3 Paper III: Pure vibrational contributions for retinal and retinal derivatives

In this paper, OpenRSP is used for the calculation of pure vibrational (PV) contributions to the polarizability and first hyperpolarizability of retinal and retinal derivatives at the DFT level. It is seen that the vibrational contributions to the first hyperpolarizability are modest if the electric field frequency is nonzero, but in the static case, the vibrational effects can be on the order of the electronic contribution. It is also seen that, in the static case, correlation effects are substantial for the pure vibrational contributions to the first hyperpolarizability. The results agree reasonably well with experiment.

3.4 Paper IV: Hyper-Raman spectra of retinal

In this paper, we use OpenRSP in the calculation of hyper-Raman spectra of *all-trans*- and *11-cis*-retinal at both the HF and DFT level. The hyper-Raman process is a spectroscopic process in the same family as Raman spectroscopy, but the selection rule deals with the first hyperpolarizability of the system under study, and not the polarizability (which is the case for Raman spectroscopy). It is seen that the Hartree-Fock results (with a DFT (B3LYP) vibrational analysis) come closest to the experimental results for the *all-trans* isomer (no experimental results were found for the *11-cis* isomer), but the good agreement at this lower level of theory is believed to be accidental. When correlation effects in the hyper-Raman intensities are included by DFT, some differences appear in the spectra. Of the DFT results, hybrid functionals seem to perform better than pure GGA functionals. There are some differences in the hyper-Raman spectra of the two isomers, but altogether, the current data suggests that hyper-Raman spectroscopy is not an attractive option for investigating isomerism in these systems.

Chapter 4

Outlook

4.1 Structural development of OpenRSP

While the main routines that make up OpenRSP are now functioning to an extent where projects like the ones in this doctoral work can be pursued, development to bring the program to a more mature form is still needed. The program in its present form is run inside the Dalton quantum chemical program[34]. Making the OpenRSP code into a standalone program will make it easier to connect it to modules that provide various information that OpenRSP needs, such as routines for 1-electron and 2-electron integral contributions, exchange/correlation contributions, response equation solver modules (this latter topic to be introduced in some more detail in Paper I), and, potentially, methodology that takes relativistic effects into consideration. Various features, such as restart options and a sufficient degree of sophistication in input/output handling, have been given a low priority thus far, but should also be pursued.

4.2 Applications

The OpenRSP program, with the current support of the integral codes, can be used for a large selection of properties. We will here make a brief mention of some of the projects that are planned or under development.

The expansion in eqn. (2.87) goes on indefinitely, and with OpenRSP, it is possible to calculate sixth-order force constants. These find some use in e.g. vibrational perturbation theory corrections to rotational constants[35]. The present OpenRSP code and associated integral codes[27] [28] [29] [30] [31] have been found to work for sixth-order force constants at the Hartree-

Fock level, and calculations on some triatomic systems are in progress.

One experimental technique involving high-order electric dipole, magnetic dipole and electric quadrupole response functions is called electric field-induced second-harmonic generation circular intensity difference (EFISHG-CID)[36] [37]. The response functions needed for a computational treatment of this technique, including the use of London atomic orbitals[38] when magnetic dipole effects are involved, could be calculated using OpenRSP. Development is still ongoing for this project, and a lower-order property involving magnetic dipole effects has been found to work at the Hartree-Fock level.

It was mentioned in Section 2.3.3 that it is possible to go beyond the double harmonic approximation for the calculation of pure vibrational contributions to polarization properties. Working expressions for this purpose have been derived[39, 40, 41], and with OpenRSP, it is possible to calculate the geometrical derivatives of polarization properties that are necessary for the evaluation of these expressions. Preliminary calculations suggest that, to a combined second order of anharmonicity in the polarization properties and the vibrational wavefunction, all necessary properties can be calculated at the Hartree-Fock level. Most of the needed properties can also be calculated at the DFT level, and work is ongoing to enable calculation of all the needed properties at this level.

Also mentioned in Section 2.3.3 were zero-point vibrational average (ZPVA) contributions. The calculation of ZPVA contributions involve geometrical derivatives of both the energy and various polarization properties. The results so far suggest that all of the necessary response properties are available at the HF level, and most of them are also available at the DFT level.

There is a large number of high-order vibrational spectroscopies for which computational work is scarce. A computational treatment of such spectroscopies typically involves high-order properties, and, with the properties that can be calculated with OpenRSP, it is possible to explore such spectroscopies in an analytic manner. Work has been started on a program for the calculation of high-order vibrational spectra.

Work has also been started on making polarizable embedding approaches such as combined quantum mechanics/molecular mechanics (QM/MM) techniques[42], including approaches where the functionality of the polarizable continuum model (PCM)[43] is included together with the QM/MM methodology[44], available to OpenRSP for a better treatment of the surroundings of a molecular system under study, which are neglected in the present version of the program. This work should enable an improved description of situations like solvation and binding at molecular interfaces.

In summary, OpenRSP can take a central position in many interest-

ing applications that involve properties that until now have been difficult to calculate, or at least may have been difficult to calculate analytically. The recursive approach used in OpenRSP is open-ended and is therefore readily extended to arbitrary-order properties given that the necessary one-electron and two-electron integral and exchange/correlation contributions are available. With the code developed in this doctoral work, we can now perform analytic calculations of novel, high-order properties of spectroscopic relevance, in time including also the effects of the molecular environment.

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Paper I

A general, recursive and open-ended response code

M. Ringholm, D. Jonsson, and K. Ruud
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Paper II

Analytic cubic and quartic force fields using density-functional theory

M. Ringholm, D. Jonsson, R. Bast, B. Gao, A. J. Thorvaldsen,
U. Ekström, T. Helgaker, and K. Ruud
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Paper III

Analytic density-functional theory calculations of pure vibrational hyperpolarizabilities: The first dipole hyperpolarizability of retinal and related molecules

B. Gao, M. Ringholm, R. Bast, K. Ruud,
A. J. Thorvaldsen, and M. Jaszuński
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Paper IV

Analytic density-functional theory hyperpolarizability gradients: The hyper-Raman spectra of all-trans- and 11-cis-retinal

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